Inhibition Pitting Corrosion of A-890-1B Stainless steel in NaCl Solution by 5-amino-1,3,4 - thiadiazole -2- thiol

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The pitting potential of ASTM A-890-1B stainless steel at different sodium chloride activities and constant temperature was studied. As sodium chloride activity increases, the pitting potential decreases, favoring localized corrosion. In addition, the effect of different 5-amino-1,3,4-thiadiazole - 2- thiol concentrations at a 3.5% NaCl concentration and constant temperature was assessed, showing that the greater the inhibitor concentration, the greater the pitting potential. In the same way, the pitting potential decreases as temperature increases in NaCl constant concentration.

1. INTRODUCTION

Pitting corrosion is a form of localized corrosion consisting in the formation of small holes in isolated spots on the metal surface.

Metallic oxide formation on metal surfaces in contact with the electrolyte protects the metal against corrosion (passivation). Several chemical species in solution attack the passive oxide film to destroy it. Pitting corrosion starts with the localized dissolution of the passive metal surface due to the attack of certain dissolved ions such as halide ions like Cl^-, Br^- and I^- that are considered aggressive [1-4].

Pitting growth generally occurs at high rates. Increases at additional temperature, weakening the oxide film,and thus pitting takes place very easily. The reason for this behavior is the higher number of limited defects localized in the passive film and the tendency to increase the oxide film in order to incorporate ions at higher temperatures [2,4-8]. Since the areas where pitting occurs are

localized, the pH inside the pitting is smaller than outside, being the oxide-reduction reactions involved in the process always the same.

A material is pitted if its electrolyte potential is greater than the pitting potential (E_{pitt}). This potential depends on material, temperature, ion nature and ion concentration in the electrolyte.

There are currently stainless steel alloys highly resistant to corrosion such as duplex steels which have a chemical composition carefully adjusted to make a mixed crystalline structure about half a ferritic phase and half an austenitic phase. This is done by incorporating a small controlled amount of nickel (sometimes Mn and N) to ferritic steel. The resulting alloy has mechanical characteristics better than those of austenitic stainless steel, allowing the use of smaller thicknesses with subsequent material saving. Its pitting corrosion resistance is very high, as it can be inferred from its pitting potential values (Epitt), thus obtaining an equivalent value for pitting resistance (PRE), between 30 and 50. ASTM 790 duplex stainless steel in a 3.5% sodium chloride solution at a 25ºC has a 900 mV$_{SCE}$ pitting potential, while ASTM 304L-type austenitic stainless steel on the same conditions has a pitting potential of about 250 mV$_{SCE}$ [8-12].

Some organic compounds have shown great effectiveness for inhibiting aqueous corrosion in a great variety of metals and alloys [12, 13]. The adsorption of these compounds is commonly explained by a film formation on the metal surface [14-18].

The 5 –amino- 1,3,4- thiadiazole -2- thiol (Bismuthiol) organic compound has been frequently used as a copper corrosion inhibitor [18-21]. These compounds react with a variety of metallic ions, forming a very fine complex polymeric layer on the metal surface, which indicates complex formation [21-25].

This paper deals with pitting on a duplex ASTM A-890-1B stainless steel surface in a 3.5% NaCl solution and its inhibition by adding 5-amino-1,3,4-thiadiazole-2-thiol . This system in corrosion has been studied determining parameters of corrosion and adsorption [24], using the electrochemical linear polarization resistance technique, 5-amino-1,3,4-thiadiazole-2-thiol corrosion current density on ASTM A-890-1B steel is determined in a 3.5% NaCl solution at different temperatures. The corrosion inhibition process is mixed. Apparent activation energy is calculated, being the one with inhibitor slightly greater than that without it. Adsorption matches Damaskin-Parsons isotherm, showing that molecules adsorbed by the metal surface reject each other. Three water molecules on the metal surface are replaced by one inhibitor molecule. This is demonstrated by calculating the surface these molecules project. Normal thermodynamic adsorption parameters are calculated, showing that the process is spontaneous and exothermic. Inhibitor adsorption on the metal surface is a chemical adsorption..

2. EXPERIMENTAL

2.1. Materials

The stainless steel Duplex ASTM A-890-1B has the following compositions in %

Table 1. Composition of steel in study

C	N	Si	P	S	Cr	Mn	Fe	Ni	Cu	Mo
0.04	0.15	1.0	0.04	0.04	25.0	1.0	bal	5.5	3.0	1.82

Pretreatment.   ASTM A-890-1B stainless steel is annealed at 400ºC for 2 h and air-cooled.

Resistance of stainless steel against pitting and crevice corrosion is improved by chromium, molybdenum and nitrogen additions. In the case of Duplex ASTM A-890-1B stainless steel it has a 33.4 PREN (Pitting Resistance Equivalent number) which makes it resistant to pitting corrosion.

The structure of the molecule of inhibitor 5-amino-1,3,4-thiadiazole-2-thiol (Aldrich 98%) used is shown in figure1.
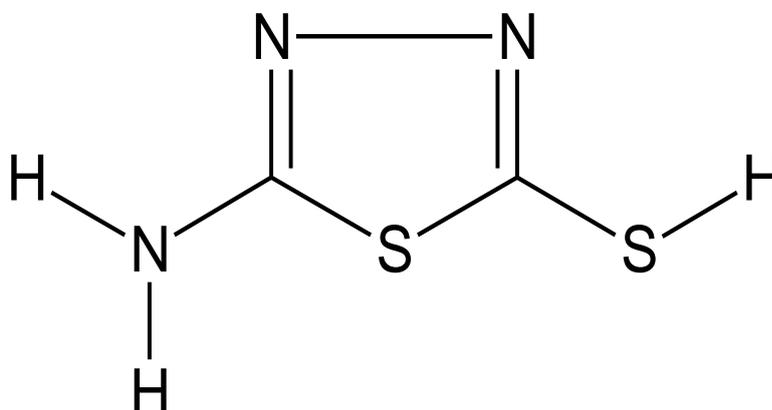
Figure 1. 5-amino-1,3,4-thiadiazole-2-thiol structure

2.2. Electrodes

The working electrode was made upon a ASTM A-890-1B pretreated cylinder which was connected to a copper conductor wire. The cylindrical part was isolated with epoxy resin, leaving an exposed area of 0.21 cm^2. Before each experiment the exposed area of the working electrode was treated with soft sand paper 3M 1500; until a metallic shine; brushed carefully; washed in abundant tap water; degreased with detergent, washed with abundant distilled water, and ethanol and finally dried with soft paper.

The reference electrode was saturated calomel (SCE), which was cleaned before each experiment to avoid contamination from the inhibitor. Distilled water was used to clean it externally; it was dried with soft paper; and some KCl crystals were kept inside, if necessary.

The auxiliary electrode was a platinum cylinder with 1.77 cm^2 of exposed surface. Before each experiment it was cleaned with distilled water, degreased with ethanol, rinsed again with bi-distilled water, and dried with soft paper.

2.3. Measurement system

To determine the pitting potential, 50 mL of electrolyte, NaCl with and without inhibitor, were introduced into the electrochemical cell and kept at constant temperature ($\pm$ 0.5ºC); the working electrode was maintained inside the cell for 5 min. After this time the auxiliary electrode was introduced into the cell in such a way that it faced (at same height) the working electrode at 2-3 mm apart. The electrolyte was sucked into the Luggins capillary and the reference electrode was placed in position. The pitting potential was determined with a potentiostate Radiometer PGZ 301 method, with which the potential varies from the resting potential to the anodic potential at a 5 mV/s scan rate until reaching 1 mA. In this moment, scanning is reversed up to 0 current.

Pitting potentials in NaCl solutions at different molal concentrations were determined: 0.01 m, 0.02 m, 0.05 m, 0.1 m, 0.5m, 0.62 m, and 1 m. at a 25ºC constant temperature.

Pitting potentials in 3.5% NaCl solutions with and without inhibitor were also determined, along with 5-amino-1,3,4-thiadiazole-2-thiol at different molal concentrations (5 x 10^{-5} M; 10 x 10^{-5} M; 20 x 10^{-5} M; 30 x 10^{-5} M; 50 x 10^{-5} M) at 25 ºC constant temperature. The pitting potential at different temperatures (20, 25,30 ,35 ,40 ,45 ,50 ºC), at a 3.5% NaCl concentration was determined.

According to the chemical analysis done, PREN (Pitting Resistance Equivalent number) was calculated with the following equation:

PREN = % Cr + 3.3 % Mo+ 16 % N

the value being 33.4, indicating that the steel is resistant to pitting corrosion and thus belongs to Duplex stainless steel.

Stable pitting is formed at a noble potential called pitting potential, E_{pitt}. This gives rise to a repassivation potential, E_{repas}, which is lower than E_{pitt}[2]. The polarization curve is loop-shaped (hysteresis). The potential at which this sloop ends on reverse scanning is the protection potential sometimes known as repassivation potential, E_{repas}. The form of the curve return determines the capacity of an alloy to repassivise [3].

3. RESULTS AND DISCUSSION

3.1 Effect of sodium chloride activity on pitting potential

Table 2. Activity of sodium chloride based on pitting potential, repassivation and its difference.

m (mol/kg)	γ^*	Activity a_{NaCl}	E_{pitt} (V_{SCE})	E_{repas} (V_{SCE})	E_{pitt}-E_{repas} (V_{SCE})
0.01	0.903	0.009	1.234	1.167	0.067
0.02	0.872	0.017	1.175	1.104	0.071
0.10	0.779	0.078	1.056	0.980	0.076
0.50	0.681	0.341	0.964	0.882	0.081
0.62	0.677	0.420	0.946	0.864	0.082
1.00	0.657	0.657	0.906	0.821	0.084

*Activity coefficients at 25°C obtained of literature [30].

The effect of the sodium chloride activity on pitting potential is attributed to the aggressiveness of halide ions. These can be adsorbed on the passive film surface, penetrating through its weak spots and pores. In this way, they destroy the film. For this reason, the renovation of the passive layer is slower, so the dissolution rate of the passive layer is higher than the repassivation rate[3,26]. Thus, as chloride activity increases, the pitting potential decreases, as shown in Table 2.

In figure 2, the anodic polarization curves shown to determine pitting potential, for different concentrations of NaCl at 298 K.
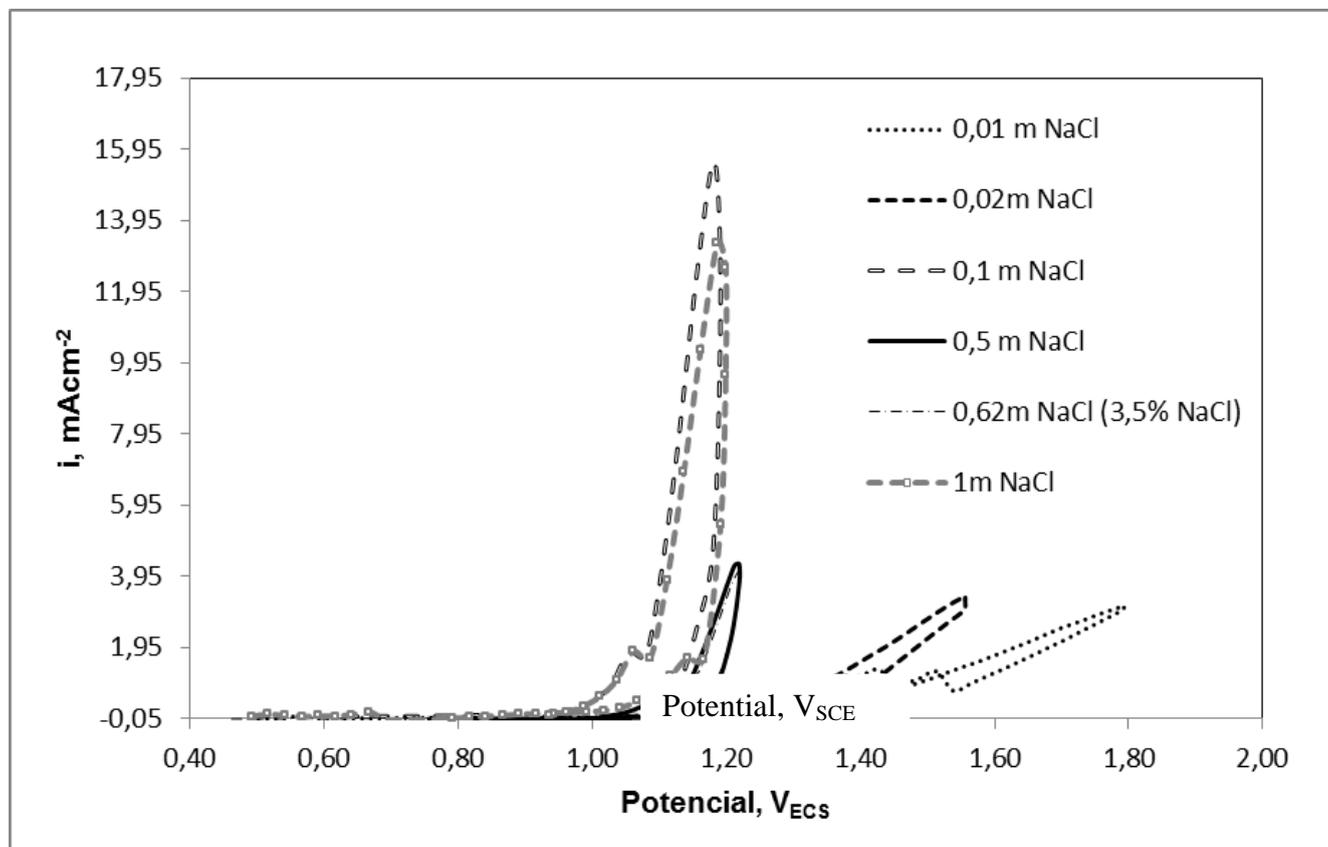

Figure 2. Pitting potential effect of different concentrations of NaCl at 298 K.

E_{pitt} y E_{repas} variation for ASTM A-890-1B stainless steel as a logarithm function of chloride activity at 25 ºC are related according to E= A - B ln a_{NaCl}, where A and B are constant. The occurrence of localized corrosion allows obtaining the following linear relation between pitting potential and repassivation potential with sodium chloride activity, figure 3:

$$E_{pitt}, V_{(ECS)} = 0.878 - 0.0741 \ln a_{NaCl} \qquad R^2 = 0.997 \qquad \text{(eq 1)}$$

$$E_{repas}, V_{(ECS)} = 0.792 - 0.0783 \ln a_{NaCl} \qquad R^2 = 0.997 \qquad \text{(eq 2)}$$

The values of slopes are 0.0741 V for E_{pitt} variation and 0.0783 V for E_{repas} with respect to the logarithm of chloride ion concentrations. This is in agreement with other authors higher values of slopes in stainless steel would be due to the formation of chlorine complexes in chrome [28-30].

The difference between pitting potential and passivation potential (eq 1 and eq 2), is obtained as follows:

$$\left(E_{pitt} - E_{repas}\right) V_{(ECS)} = 0.792 - 0.0783 \ln a_{NaCl} \qquad R^2 = 0.994 \qquad \text{(eq 3)}$$
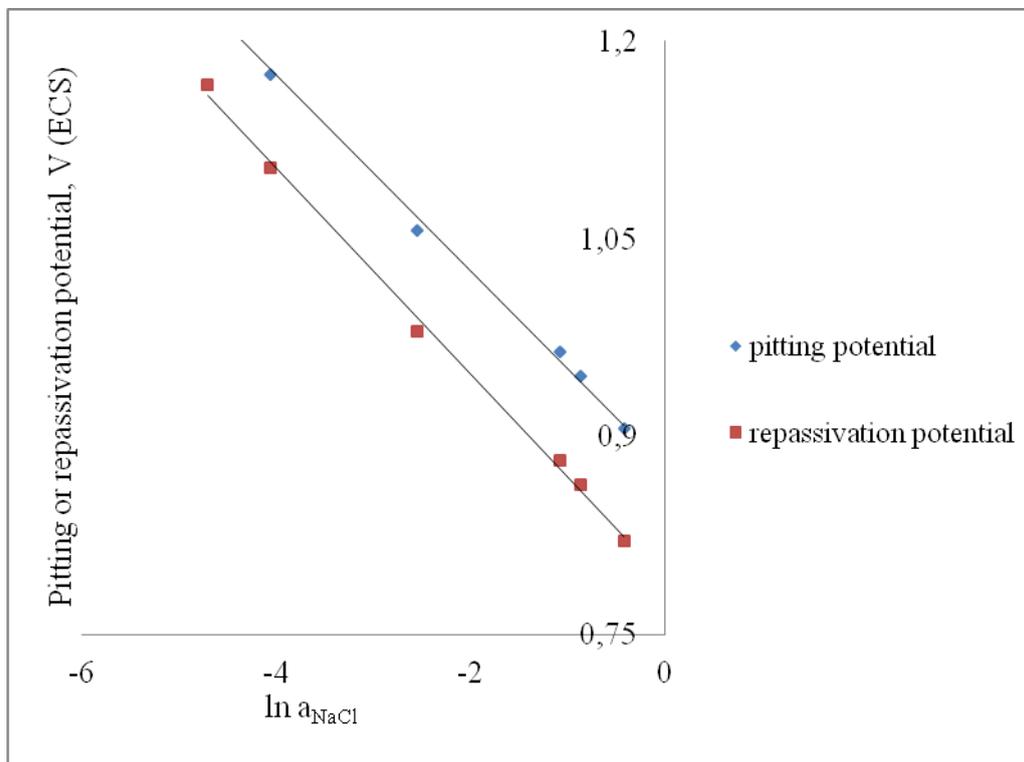
as shown in figure 4.

Figure 3. Pitting potential and repassivation potential with respect to the activity of sodium chloride for ASTM A-890-1B stainless steel at 25ºC.
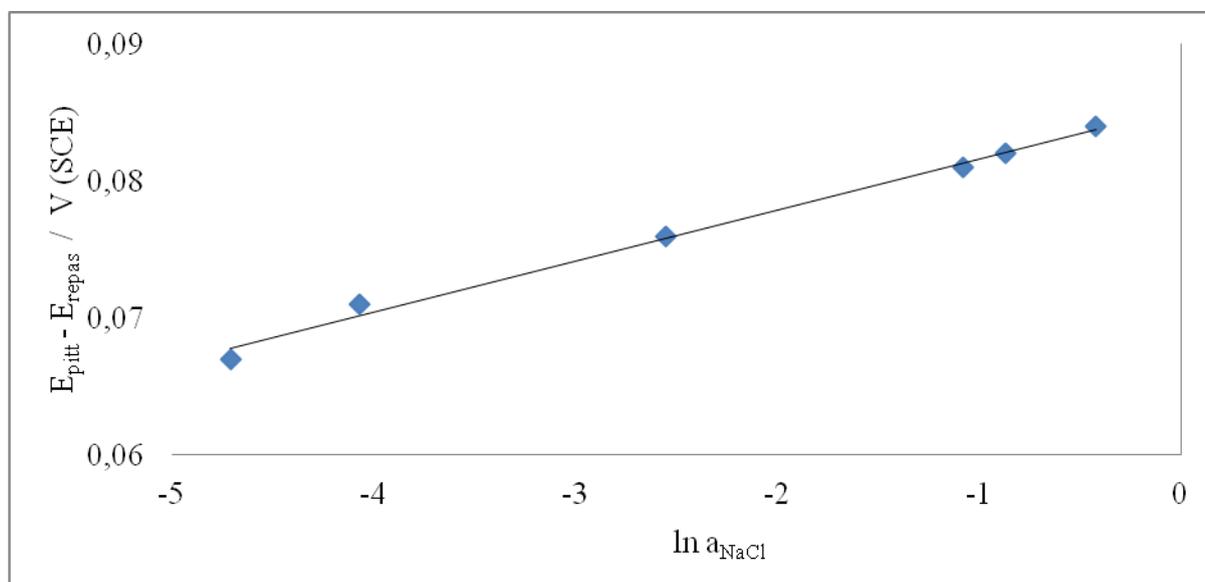

Figure 4. Difference between E $_{pitt}$ and E $_{repas}$ with respect to the activity of sodium chloride for ASTM A-890-1B stainless steel at 25ºC.

where, as sodium chloride activity increases, the difference also increases; thus, the alloy takes larger to repassivation.

Figure 5, shows the ASTM A-890-1B steel surface before and after the pitting potential experiment. Small pitting on the surface is clearly shown, indicating the chloride effects and why it called localized corrosion.
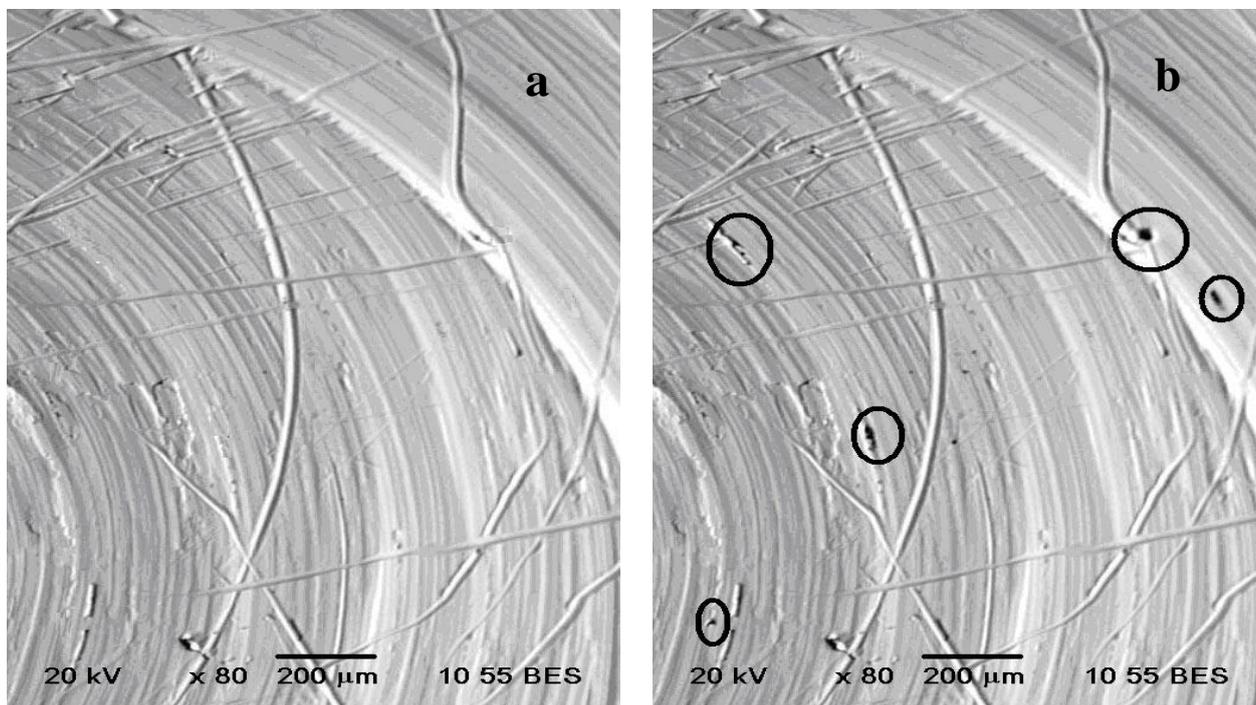

Figure 5. Micropictures of ASTM A-890-1B steel surface using an Electronic microscope Aldrich 1055 BES, a) before immersion, b) after immersion in 3.5% NaCl for 90 minutes.

3.2 Inhibitor effect

The effect of adding different concentrations of 5-amino-1,3,4-thiadiazole-2-thiol inhibitor on the pitting potential value is shown in Table 3:

Table 3. Variation of the E_{pitt}, and E_{repas} and its difference in the presence of different 5-amino-1,3,4-thiadiazole-2-thiol concentrations,

Concentration, 10^4, M	E_{pitt}, $V_{(SCE)}$	E_{repas}, $V_{(SCE)}$	E_{pit}-E_{repas}, $V_{(SCE)}$
0.5	1.148	1.127	0.022
1.0	1.154	1.088	0.066
2.0	1.158	1.049	0.109
2.5	1.160	1.040	0.120
5.0	1.165	1.001	0.164

Figure 6, shows the relation between E_{pitt} and the logarithm of the molar concentration of the additive.
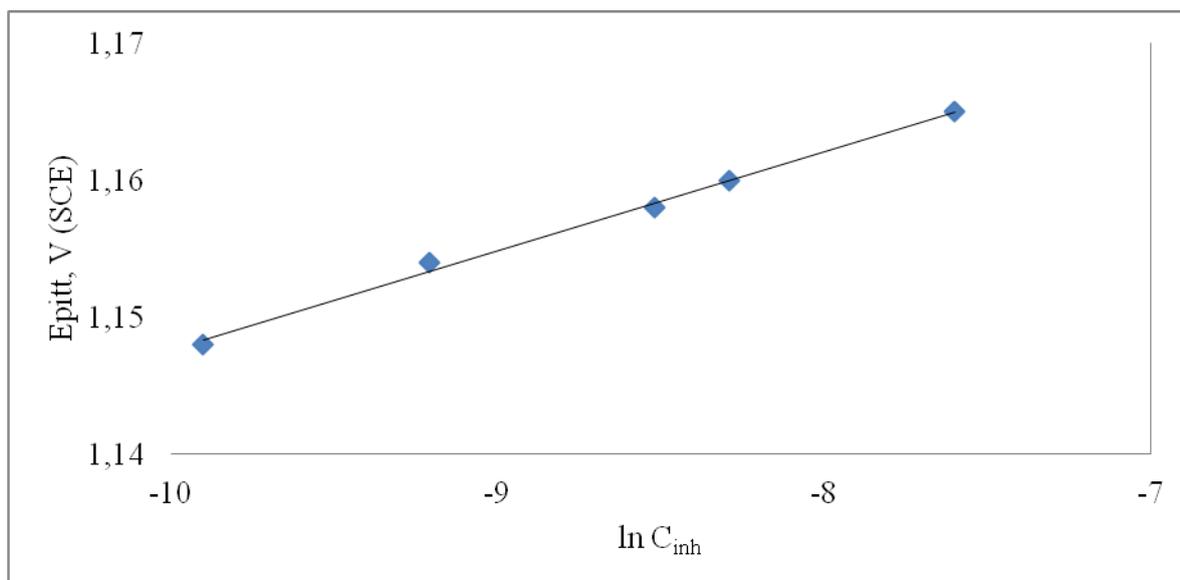

Figure 6. Relation between ASTM A890-B steel pitting potential and the logarithm of several additive concentrations in the presence of 3.5% NaCl.

This figure shows that as inhibitor concentration increases, pitting potential increases, sometimes changing to more positive values according to equation:

$$E_{pitt}, V_{(SCE)} = 0.0072 \ln C_{inh} + 1.22 \qquad (eq4)$$

The 5-amino-1,3,4-thiadiazole-2-thiol inhibitor contains nitrogen and sulfur in its structure, which produces better inhibiting properties. This is attributed to its molecular structure. Planarity and the pairs of free electrons in the heteroatoms are important features that determine the adsorption of these molecules on the metal surface [22-25].

3.3 Temperature effect

Pitting potential determination was made at different temperatures (20, 25, 30, 35, 40, 45, 50 ºC) at 3.5% NaCl. Temperature increase on the solution causes E_{pitt} to change into an active direction, indicating a tendency toward pitting increase [26-28].

Table 4 and figure 7 shows the effect of temperature on the pitting potential:

This table shows how temperature increase causes E_{pitt} to decrease.

The gradual decrease of the pitting potential with increasing temperature has been ascribed mainly to the enhanced dissolution kinetics of the metal (increase in corrosion current density in the pit environment). However in deep pits or crevices there will also be effects on the critical environmental conditions [29].

Table 4. ASTM A890 pitting potential at different temperatures in the presence of 3.5% NaCl

Temperature (K)	Pitting Potential $V_{(SCE)}$
293.2	1.102
298.2	1.098
303.2	1.068
308.2	0.998
313.2	0.860
318.2	0.675
323.2	0.429

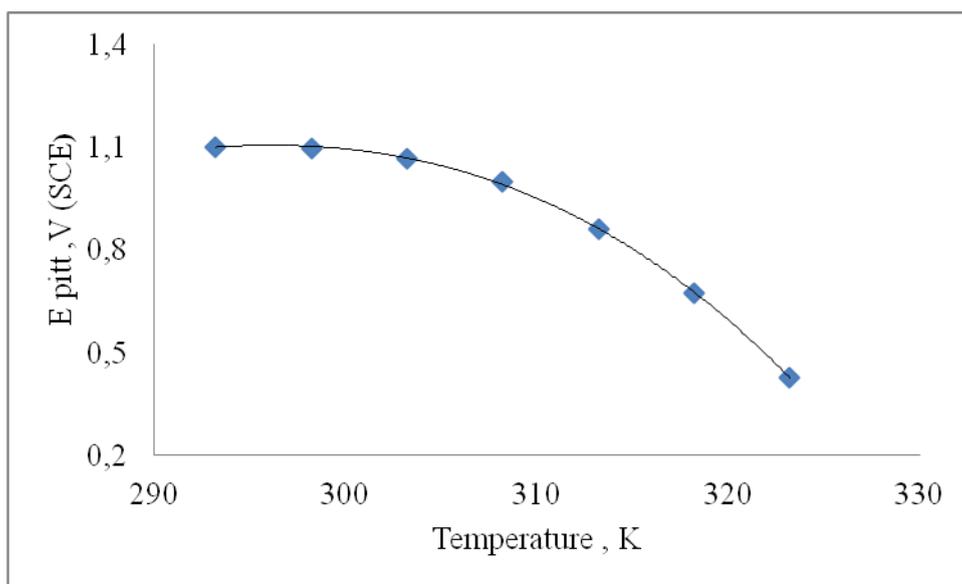**Figure 7**. Relation of pitting potential temperature of ASTM A890-B stainless steel.

$$E_{pitt}, V_{(SCE)} = -9.33 \ 10^{-6} \ T^3 + 7{,}62 \ 10^{-3} \ T^2 - 2.06 \ T + 1.85 \ 10^2 \quad R^2 = 1{,}00 \qquad \text{(eq5)}$$

Solution temperature and chloride ion concentration decrease the formation rate of the oxide layer on the metal surface. This process is accompanied by a considerable decrease of Epitt [3,30-33].

4. CONCLUSIONS

At constant temperature, if chloride activities increase, decreases the ASTM A-890-1B stainless steel pitting potential.

At constant temperature, if inhibitor concentrations increase, increases the pitting potential.

At constant NaCl concentration, the pitting potential decrease as temperature increases, with or without inhibitor.

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